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13. ABSTRACT We carried out a study to determine the feasibility of electrochemically removing chromium from plating wastewater. Hexavalent chromium is a carcinogen and its discharge is required to be near 1 ppm. In our work we determined the effects of key variables including temperature, electrolyte flow rate, pH, and electrode composition. At the low chromium concentrations found in plating wastewater, we determined that the rate of chromium ion removal was mass transfer limited. Of the four electrode types tested, only gold gave significantly enhanced performance; however, graphite would probably be the most cost-effective for large-scale application. Chromium reduction rate was significantly increased at reduced pH. Because chromium ion solubility increases at lower pH, the higher removal rate would need to to be balanced against higher chromium redissolution rate in a practical system. A preliminary analysis based on our laboratory data indicates that a practical system based on electrochemical technology is feasible.

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Contents

1 Statement of the Problem

Untreated chromium wastewater from plating operations is an environmental hazard. Because hexavalent chromium ions have been shown to be carcinogenic, federal and local authorities regulate the maximum permissible chromium ion discharge into waterways. Chromium plating is carried out at several Army facilities, where chromium ion concentrations from wastewater are reduced through chemical treatment. Although exact discharge requirements are regulated by local authorities, permissible discharge concentrations are on the order of several parts per million. Our objective was to determine whether an electrochemical chromium removal process was feasible for treating plating wastewater and had the potential to reduce chromium ion concentrations to the required levels.

2 Summary

We carried out a study to determine the feasibility of electrochemically removing chromium from plating wastewater. Previous investigations revealed that hexavalent chromium ions could be reduced electrochemically to the trivalent form and precipitated on an electrode in basic solution to an insoluble hydroxide. In our work we determined the effects of key variables including temperature, electrolyte flow rate, pH, and electrode composition. At the low chromium concentrations found in plating wastewater, we determined that the rate of chromium ion removal was mass transfer limited. Of the four electrode types tested, only gold gave significantly enhanced performance; however, this material would be impractical for large-scale

application. Chromium reduction rate was significantly increased at reduced pH. Because chromium ion solubility increases at lower pH, the higher removal rate would need to to be balanced against higher chromium redissolution rate in a practical system. A preliminary analysis based on our laboratory data indicates that a practical system based on electrochemical technology is feasible.

3 Introduction

The current technology for reducing chromium ion concentrations in plating wastewater is based on chemical technology. Hexavalent chromium ions can be removed from wastewater by reduction of the chromate ion to trivalent chromium with chemicals such as SO_2 or $FeSO_4$. Chromic ion is then precipitated as a hydroxide by raising the pH [1].

The chemical technology is currently used at the Letherkenny Army Depot in Chambersburg, PA. According to Mr. Dennis Reed, who is in charge of plating operations at Letherkenny, typical rinsewater contains chromium in the range of 10 ppm. The daily maximum discharge concentration permitted by state authorities is 2.77 mg/L total chromium and 0.068 mg/L hexavalent chromium. Monthly average discharge concentrations at about half these levels are permitted.

Because the trivalent chromium ion is less hazardous, techniques for plating from these baths have been proposed. Until recently, all chromium deposition processes were based on a direct reduction of the hexavalent species, but recently a bath based on mostly trivalent chromium has been proposed [2]. The trivalent species is more strongly hydrated, and the bound water makes reduction to metallic chromium more difficult [3].

Removal of hexavalent chromium by adsorption on activated carbon is not sufficiently effective to be considered for large scale applications [4]. A more promising technique for chromium removal from plating wastes is based on reduction of chromium ions through an initial electrochemical step. Because the mechanism of reduction is complex, poor control of operating conditions leads to inefficient chromium removal from a wastewater stream. In one process, electrodeposition of chromium on a reticulated vitreous carbon cathode was proposed [5]. On a bench scale apparatus, only 50% of the chromium was removed after ten passes through the electrochemical cell. Such a low efficiency would be inappropriate for large scale metal removal. The basis of a more promising electrochemical technique has been discussed by Golub and Oren [6]. They proposed the reduction of hexavalent chromium ion to chromic ion followed by treatment at high pH to form an insoluble chromic hydroxide. In initial electrochemical experiments, they demonstrated high efficiency of chromium removal on graphite electrodes.

The basic electrochemical reaction is

$$CrO_4^{2-} + 4H_2O + 3e = Cr^{3+} + 8OH^-$$ (1)
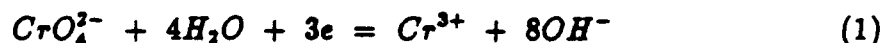
As mentioned above, the trivalent chromium ion cannot be easily removed by direct

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deposition of metallic chromium on the cathode. Instead, if the pH is sufficiently high, an insoluble hydroxide can be formed.

$$Cr^{3+} + 3OH^- = Cr(OH)_3 \qquad (2)$$
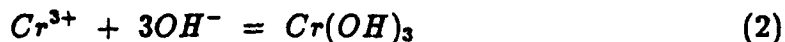
A technique for promoting precipitation is to carry out the process in a porous electrode held at relatively negative potentials (near -1.3 V vs. Hg/HgSO$_4$). In initially acidic solution the hydrogen evolution reaction increases the local pH.

$$2H^+ + 2e = H_2 \qquad (3)$$

In a porous electrode the reduction of hydrogen ions leads to a local increase in pH, which could be maintained through control of operating conditions (flow rate and electrode potential). In more basic solution the corresponding cathodic reaction is

$$2H_2O + 2e = H_2 + 2OH^- \qquad (4)$$
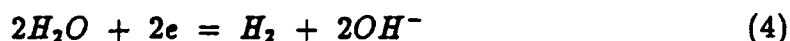
This reaction also raises the local pH. The solubility minimum for chromic hydroxide is in a pH range between 6 and 8. Removal of the chromium from the electrode could be carried out by raising the electrode potential in a separate operation.

An entirely electrochemical operation would be attractive from several perspectives. The electrodes could be fabricated from inexpensive graphite-based material, which would have a long service life. A properly designed system would be versatile and accept a range of chromium wastewaters. Variations in feed streams could be accommodated through potential and feed rate control. The pH changes inside the porous electrodes could be regulated through control of the process variables, and no additional chemicals would be required.

4 Experimental

Experiments were performed on a rotating disk electrode system (Pine Instrument ASR with Model AFDTI36 disk assembly). Disks were 0.5-cm diameter. Potential was measured with respect to a Hg/Hg$_2$SO$_4$ reference electrode. Temperature was controlled to within 0.5°C with a Thermomix 1480 thermostat. The working electrode compartment was custom-built from a 3 L Teflon beaker with an electrolyte solution volume of approximately 1 L. All electrolyte solutions were prepared from analytical grade reagents and 10 MΩ-cm de-ionized water.

5 Results and Discussion

We studied the effects of the significant variables including temperature, fluid flow, electrode composition, and pH. Studies were carried out under base-case conditions (Table 1), unless otherwise indicated. All curves from our study were generated on a rotating-disk electrode.
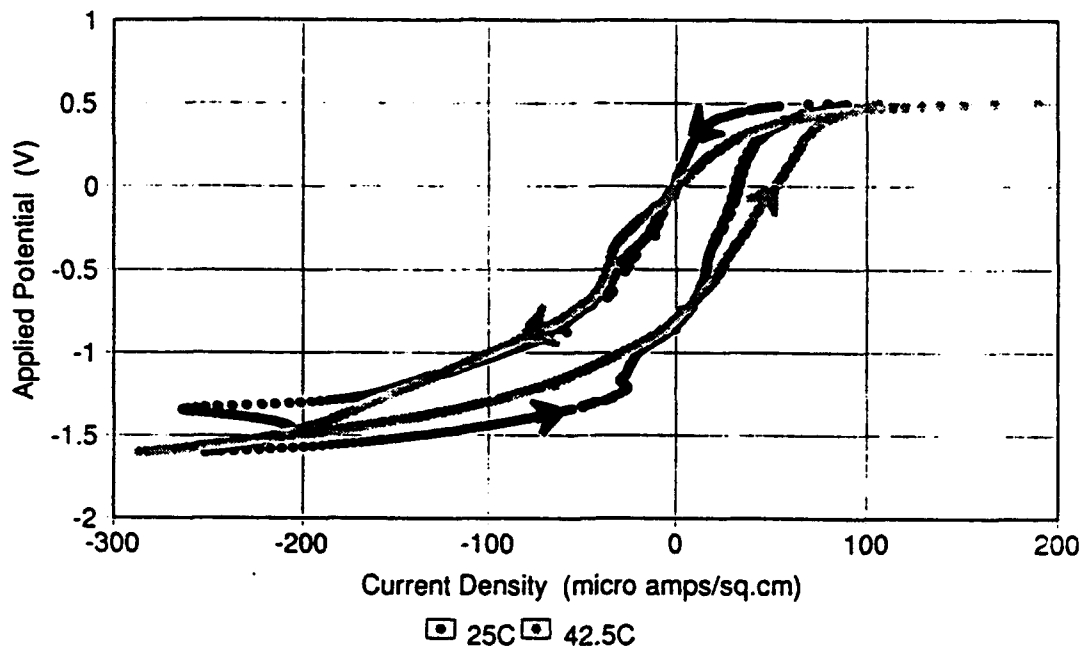
Temperature Comparison

Figure 1: The effect of temperature on chromium ion reduction near room temperature is small. The second scan on graphite is shown in each case under base conditions.

Parameter	Value
Temperature (°C)	25
pH	3.2
Chromium ion concentration (ppm)	250
Disk rotation rate (rpm)	2000
Voltage sweep rate (mV/s)	2

Table 1: Base-case conditions for chromium reduction on a rotating disk electrode.

Effects of temperature appear in Fig. 1. In the 25°C - 42°C range current density is not significantly affected near the chromium reduction maximum (near -600 mV vs. Hg/Hg_2SO_4). This result indicates that a process would not be expected to be temperature sensitive in a range near room temperature.

The effects of rotation rate on the reduction of chromium ions appear in Fig. 2. Current increases with rotation rate, indicating a mass-transfer limitation. The more rapid rotation rate draws fluid to the disk surface in a predictable manner. Increased rotation rate corresponds to an increase in stirring or fluid flow. According to the Levich equation [7] a mass-transfer limited system should exhibit a linear dependency between the square root of the rotation rate and the limiting current density for the electrode process (chromium ion reduction). Although there is significant scatter in the data, our results show a definite trend. The effect amounts to a 50% increase in current as the rotation rate increases from 500 to 3500 rpm.

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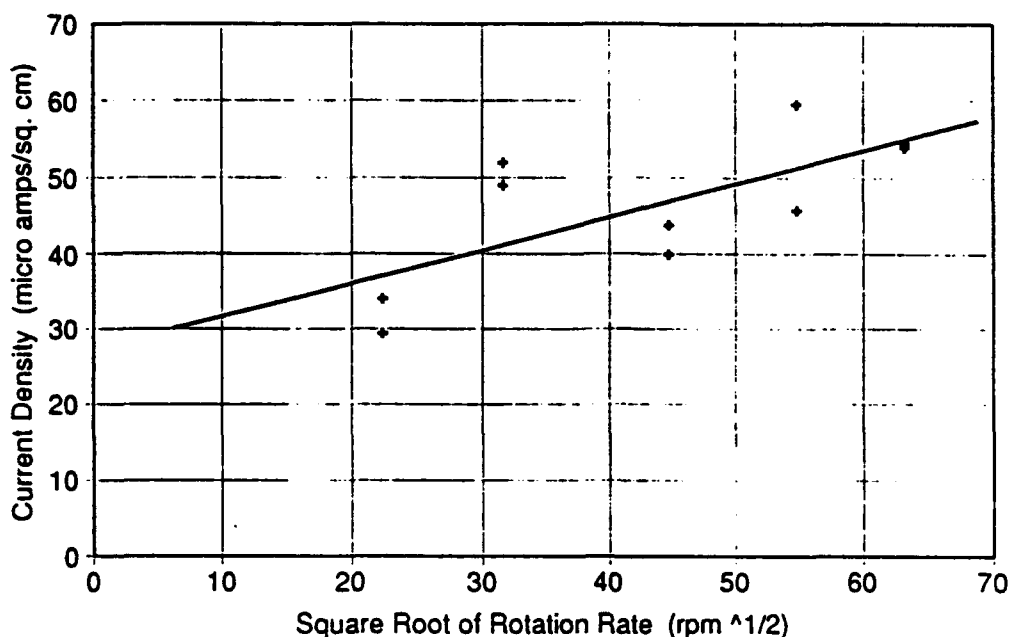## Current Density vs. Rotation Rate

Figure 2: Current Density at the chromium reduction peak (~600mV vs. Hg/Hg2SO4) is mass transfer limited. The data shown was taken under base conditions on a graphite electrode.

This result implies that in a practical system increased stirring or fluid flow would be advantageous.

We compared the chromium removal capability of several electrode materials including graphite, aluminum, a Dimensionally Stable Anode (DSA), and gold. The DSA is used commercially to oxidize the chloride ion to chlorine in the chlor-alkali process. The DSA electrode results shown in Fig. 3 indicate no significant advantage over graphite near the chromium reduction maximum (-600 mV vs. Hg/Hg_2SO_4). A disadvantage of the DSA is that it promotes the evolution of hydrogen at more negative potentials. Hydrogen evolution is a parasitic reaction that consumes electrical energy; the increase of this reaction would reduce the efficiency of a practical system.

To determine whether the electrode surface changes significantly with over time, we cycled the potential of the graphite electrode. Large differences in chromium reduction capability, as evidenced by changes in the current-potential curves (voltammogram), would indicate an alteration of the electrode surface. We found that the voltammogram tends to stabilize after the second scan. A comparison between the first and fourteenth scan reveals that differences in chromium reduction capability is minimal (Fig. 4). Although electrode degradation would need to be judged in longer term tests at the chromium reduction potentials, these preliminary results are encouraging.

Most materials performed within a narrow range in terms of the maximum chromium reduction at the current peak, near -600 mV vs. Hg/Hg_2SO_4. The performance of the gold electrode was exceptional. As shown in Figs. 5 and 6, the
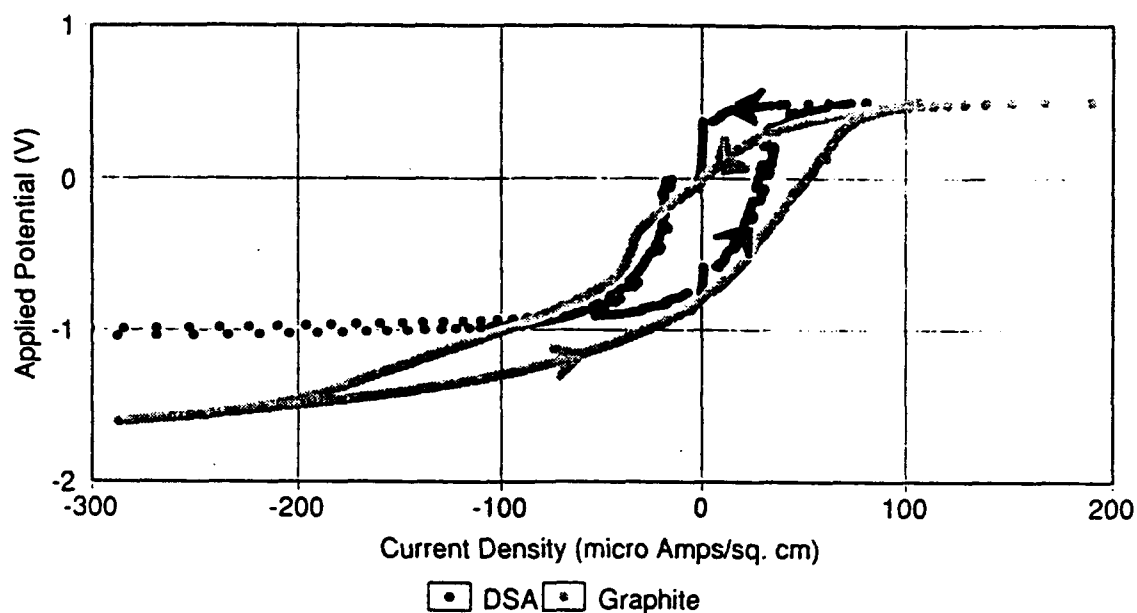
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Comparison of DSA and Graphite

Figure 3: The DSA anode does not display the expected chromium reduction peak (~-600 mV vs Hg/Hg2SO4) and evolves hydrogen at higher potentials than does graphite. Second scan and base conditions for both electrodes.
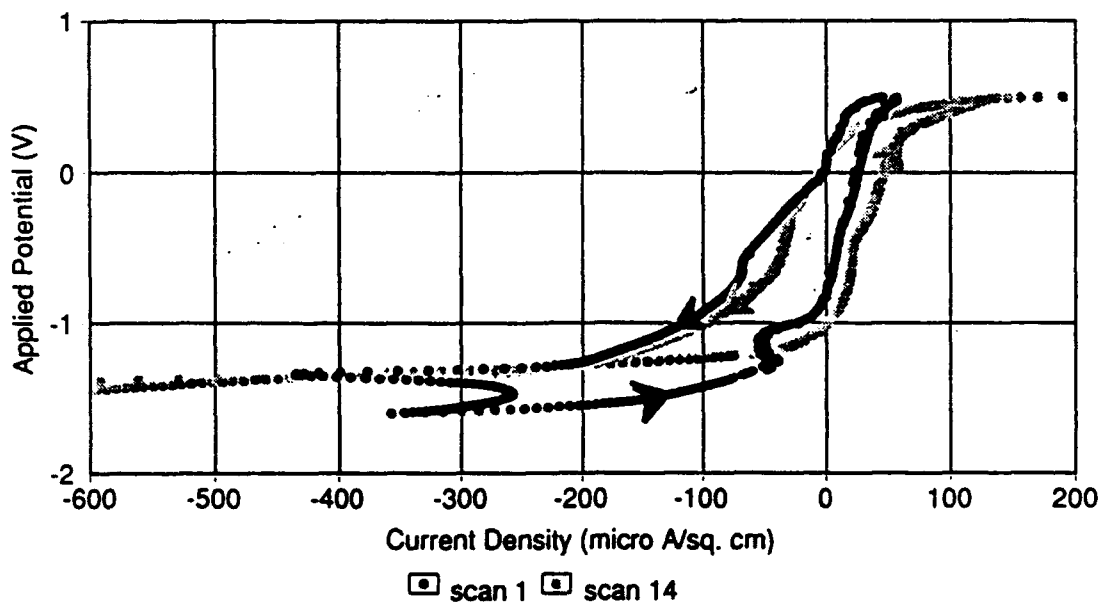
Scan vs time

Figure 4: The effect of multiple scans on a graphite electrode under base conditions. There is a reduction in the chromium peak (~600mV) that is stable after the second scan.
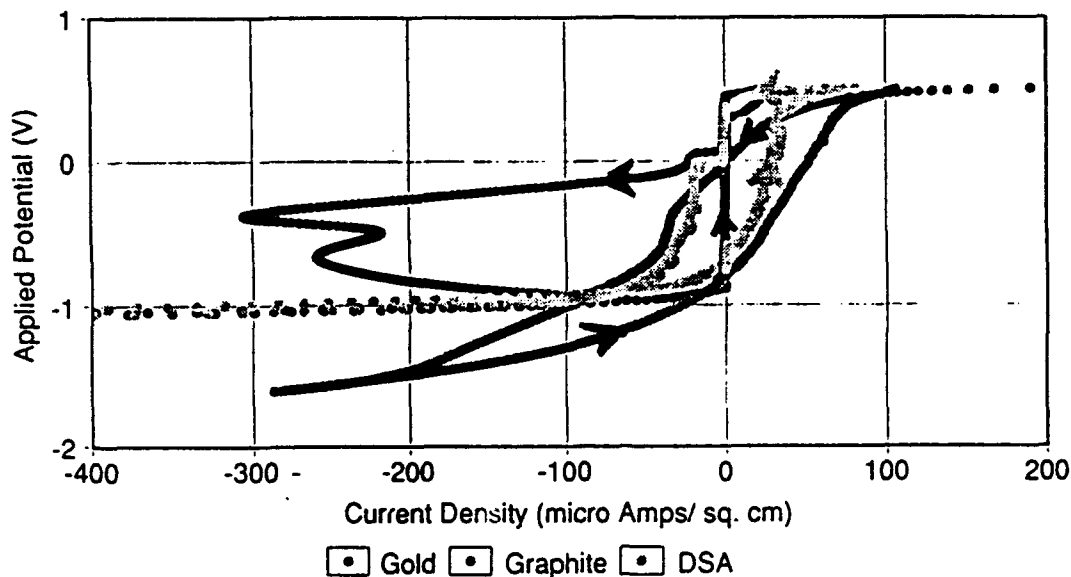
Comparison of Electrode Materials

Figure 5: Gold electrode displays the highest chromium conversion peak (~600 mV vs Hg/Hg2SO4) of the materials examined. Scans are from second scan under base conditions.

current at the chromium reduction peak was approximately five times greater than for the graphite electrode.

The results of additional scans are shown in Fig. 7. The increased reduction current appears to be stable and maintains the relative advantage over graphite after four scans. We do not currently have an explanation for the greater effectiveness of the gold electrode. Because of cost, gold would be an unlikely candidate for adoption in a large-scale system; however, these experiments illustrate the potential that other materials may have for application.

Solution pH strongly affects the chromium reduction current. Fig. 8 shows that the current increases by an order of magnitude as the pH is lowered from 4 to 3. In a practical system the increased current at lower pH would need to be balanced against the increased solubility of chromium ions as the pH is moved from neutral values, where the solubility is a minimum. To some extent the near-surface electrode pH would be raised by the reduction of hydrogen ions; however the extent to which a higher near-surface pH could be maintained has not been established. Also, the reduction of hydrogen ions requires additional current, which would reduce the efficiency of a process.

We estimated the amount of hydrogen evolution at each potential by using electrolyte containing no chromium; therefore, at each potential the current is due to parasitic reactions, in this case hydrogen evolution. At the chromium peak, under base-case conditions, the fraction of parasitic current varies with pH. At pH 4, the percent of total current involved in hydrogen evolution is approximately 20%. At
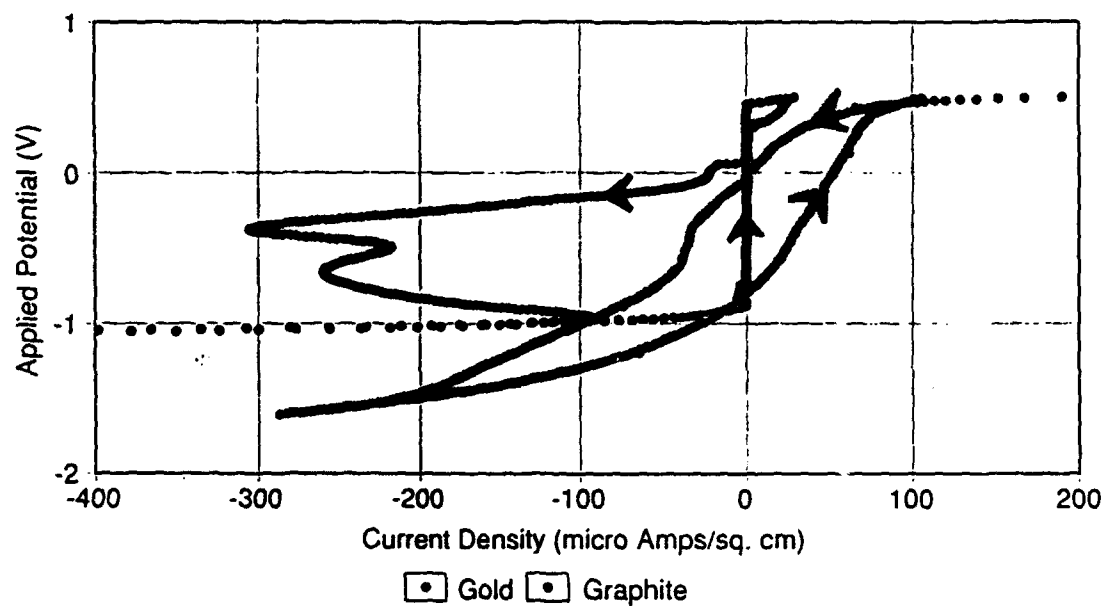
Comparison of Graphite and Gold

Figure 6: Gold displays a much larger chromium reduction
peak (~600 mV vs Hg/Hg2SO4) than Graphite. Second
scan under base conditions is shown in both cases.

Effect of Multiple Scans on Gold
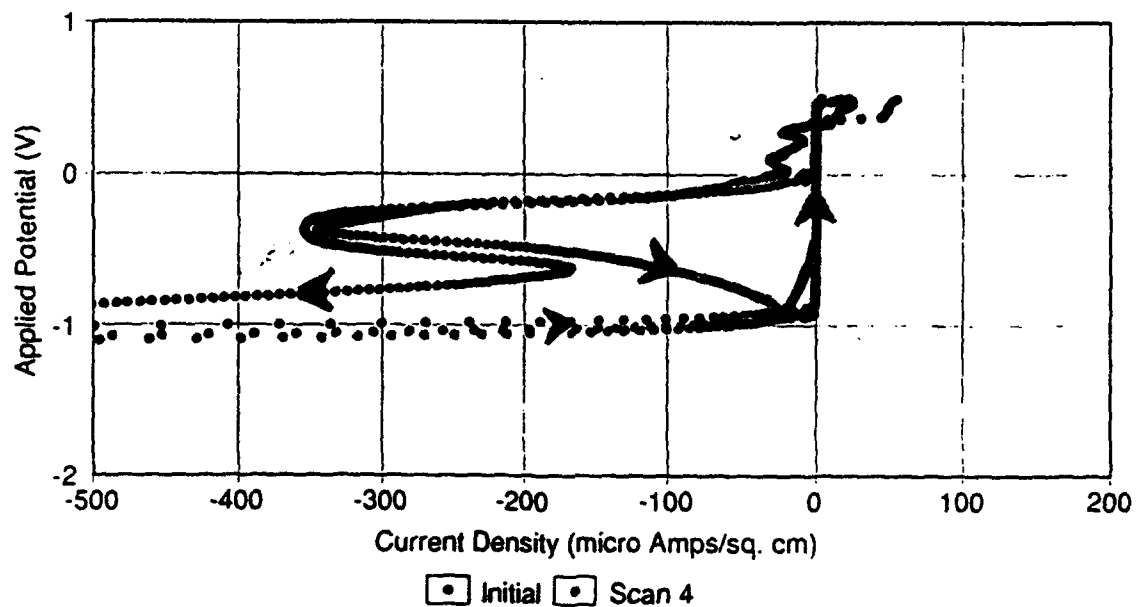

Figure 7: Gold shows negligible reduction in the chromium
reduction peak (~600 mV vs Hg/Hg2SO4) even after repeated
scans. Curves represent data taken under base conditions.

Effect of pH on Cr (VI) reduction peak
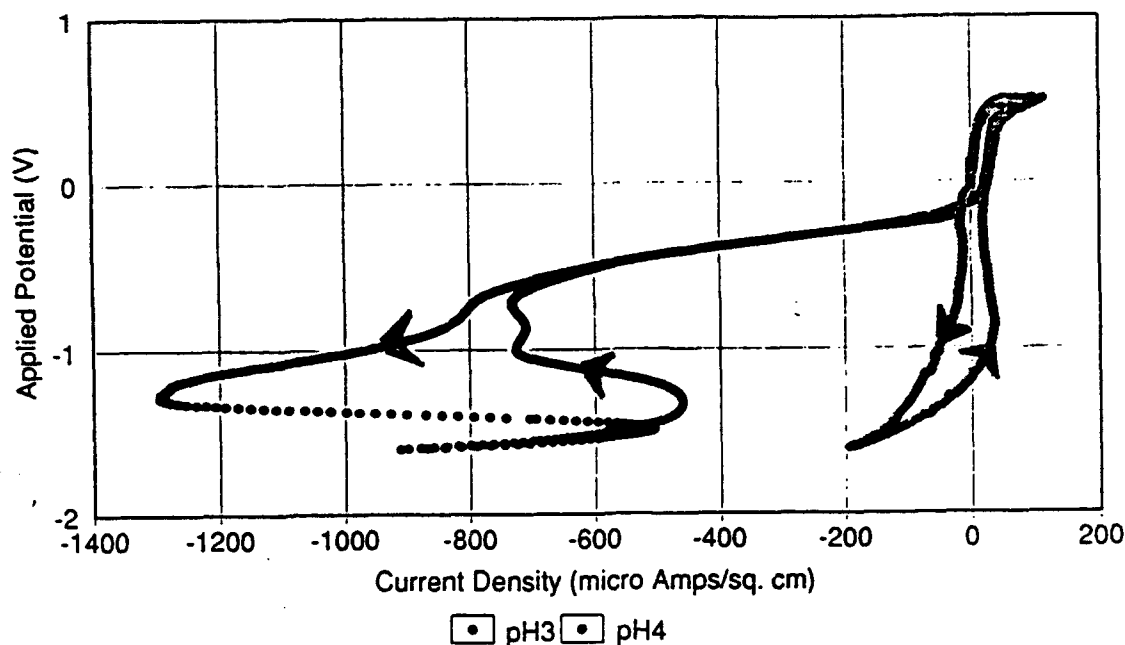

Figure 8: The chromium reduction current (at ~ -600 mV) is significantly affected by solution pH. Results are from the second scan on each electrode under base conditions.

pH 3 the parasitic current drops to 5% of the total. In these calculations, we have assumed that the parasitic current remains at the levels when no chromium was present.

Total current densities and parasitic current densities as a function of pH are summarized in Table 2. The table also shows that the potential maximum varies with pH. From these data we can estimate the rate at which chromium can be removed. From Faraday's law, the mass of chromium removed per unit time per unit of electrode area m is given by

$$m = \frac{Mi}{nF} \tag{5}$$

$$= 1.8 \times 10^{-4} i \quad g/s - cm^2 \tag{6}$$

where M is the atomic weight of chromium (52 g/mol), n is the number of electrons participating in the reaction (3), F is Faraday's constant (96,500 C), and i is the current density (A/cm^2). At pH 3, $m = 1.5 \times 10^{-7}$ g/s-cm^2.

From this calculation we can determine the electrode area required to treat a specified quantity of wastewater. For example, if we want to treat 1000 L/h of wastewater containing 10 ppm chromium, we can calculate that about 20 cm of electrode area would be required. This electrode area for the quantity of wastewater treated is fairly modest and would certainly be feasible in a large-scale process. We have assumed that the current density could be maintained and that redissolution of the chromium would not occur to an appreciable extent.

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Solution pH	pH 2	pH 3	pH 4
Potential maximum (mV)	-625	-700	-300
Total current density (μA/cm^2)	-3000	-900	-100
Parasitic current density (μA/cm^2)	-40	-50	-20

Table 2: Current density on a rotating disk electrode at selected pH values

6   Conclusions

The results of this study indicate that the removal of chromium from low concentration wastewater by an electrochemical process is technically feasible. Of the electrode materials tested, inexpensive graphite appears to be the most appropriate for large-scale processing. Although electrodes fabricated from gold gave superior technical performance, the cost could probably not be justified in a large-scale process. Near room temperature, modest changes in temperature do not adversely affect process efficiency. Our study showed that mass transfer limitations govern the rate of chromium removal; consequently, it would be advantageous to operate a scaled-up system with vigorous stirring. The rate of chromium reduction was shown to be sensitive to solution pH. Although the rate increased with decreasing pH, the solubility of chromium also increases at lower pH. This result indicates that a large-scale process should probably be operated at an intermediate pH, reflecting a balance between these competing effects.

7   Directions for Future Research

Prior to consideration of an electrochemical system for chromium removal, several additional laboratory investigations should be carried out. Removal of the precipitated chromium from the electrode was not addressed in this feasibility study. It should be possible to remove concentrated chromium by reducing the pH and possibly biasing the electrode in the positive direction, thereby increasing the dissolution rate.

Long term electrode stability should also be investigated. In this study we cycled the electrodes through several dozen potential variations. The question of electrode lifetime could best be addressed through long-term tests of the electrodes at fixed potentials. Long-term tests would also be useful in determining the rate of chromium removal at lower concentrations.

8   Personnel and Publications

Two students worked on this project. Todd Wilson obtained a Master's degree in chemical engineering while working on this project; he is now working at Geocenters, Inc. in Aberdeen, MD. Christine Walker was a senior while working on this project.

She is currently an engineer at the research center of W. R. Grace in Columbia, MD. We have not submitted a manuscript for publication or patent purposes.

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